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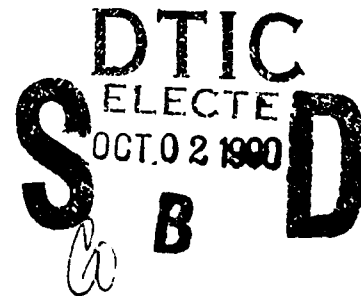
FACEPIECE MATERIAL SURVEY

AD-A227 015

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ABSTRACT

A survey was carried out to suggest materials or processes which can improve chemical warfare agent (CWA) resistance while maintaining physical properties for a facepiece application. Adhesive bonding to silicone, coating/surface modification of silicone, coprocessing with silicone, alternative designs, and alternative materials were reviewed. With only limited CWA resistance information available, and alternative design using currently available materials appears to be the best selection to meet the facepiece criteria.

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INTRODUCTION

The criteria for a good facepiece material are: good chemical warfare agent (CWA) resistance, "wearability," and good aging/storage behavior. These facepiece criteria depend on both the inherent material properties and how the design incorporates these materials. The CWA resistance and aging/storage behavior are essentially material properties, whereas wearability is more subjective. This equates to a material which is easily removed from storage and comfortably put on, worn, and removed over the temperature range to be encountered (-25°F to 120°F). Much of this would depend on design, as well as the materials used. Wearability implies the use of an elastomeric material in order to conform to the head/face to isolate the soldier from the field environment.

CWA resistance was considered the most important factor in material selection. HD and GD resistance were recently reported for a broad range of elastomers.¹ While these data represent the behavior of specific formulations, they were generally used to initially screen polymer types for resistance behavior. Butyl, chlorobutyl, and fluoroelastomers all showed excellent resistance while silicone and fluorosilicone showed extremely poor resistance.

Tensile strength, elongation, tear strength, hardness, and other physical properties are considered as a combination of quantitative properties which define wearability. The engineering specifications in Table 1* reflect these expected requirements for the facepiece material. Silicone, fluorosilicone, natural rubber, and neoprene elastomers all maintain the low temperature flexibility properties considered essential to wearability. However, the natural rubber and neoprene typically contain additives which make them unacceptable for skin contact. The elastomers with good CWA resistance are considered too "stiff" for good wearability.

Table 1. ENGINEERING SPECIFICATIONS FOR THE FACEPIECE MATERIAL

1. Physical and Mechanical Properties				
Properties (RT)	Units	Minimum	Maximum	Test Method
Tensile Strength	psi	1400	4200	ASTM D 412
Elongation	Percent	400	900	ASTM D 412
Tear Strength (Die C)	lb/inch	200	---	ASTM D 624
Hardness	Shore A	40	60	ASTM D 2240
Resilience, Bashore	0 to 100	60	---	ASTM D 2632
Bend Recovery (-25°F)	Degrees	40	---	MTL Method
Blocking		8 (sticking) 10 (mottling)		ASTM D 3003 (Modified)
Tension Set	Percent			ASTM D 412
Compression Set	Percent	---	15	ASTM D 395
Ozone Resistance		80	---	EA Dir 618-78
2. Coating Properties (if applicable)				
Adhesion	lb/2 inches width	4	---	ASTM D 751
Abrasion	mg/rev.		Pass*	ASTM D 3389 Method B [†]

*No evidence of substrate

†CS-10F wheel, 500 g load, 500 cycles

*GROVE, C. Memorandum for Record

1. SEGERS, D. P., and SPAFFORD, R. B. *Immersion and Permeation Testing of Chemical Agent Polymers*. Southern Research Institute Contract DAA646-82-C-0079, Final Report, MTL TR 87 60, 1987.

Polymers containing unsaturation in their molecular structure are subject to poor aging/storage characteristics. The additives associated with natural rubber and neoprene are typically antiozonants and antioxidants necessary for maintaining long term physical properties. Without these additives long term aging/storage behavior is poor. Silicone, fluorosilicone, butyl, chlorobutyl, fluoroelastomers, and ethylene/propylene elastomers all show good aging/storage behavior.

No one type of polymer thus appears able to fulfill all the criteria for facepiece material. Guidelines that this material must be implemented into 6.3 by FY1994 would seem to preclude the development of new materials of the possible use of experimental materials. A good facepiece material must come from a combination of available materials in a useful design. The main purpose of this survey is to suggest materials or processes which can improve CWA resistance while maintaining physical properties. The approaches listed here are primarily aimed at incorporating the silicone polymers, for their good mechanical properties, in a way in which the poor CWA performance is not a factor. Adhesive bonding to silicone, coating/surface modification of silicone, coprocessing with silicone, alternative designs, and alternative materials were reviewed and are summarized below.

ADHESIVE BONDING TO SILICONE

Improvement in CWA resistance may be achieved by adhesive bonding a resistant material to silicone. Due to their excellent CWA resistance, butyl rubber and fluoroelastomers are two of the most promising materials for lamination onto polymers based on dimethyl siloxane (silicone) to form the final facepiece material. Based on the Adhesive Bonding Data Base (ABDB), which is part of PLASTEC at Picatinny Arsenal, a number of adhesive bonding handbooks and monographs,²⁻⁹ and discussions with adhesive bonding experts,¹⁰⁻¹¹ the bonding of each of these materials onto silicone rubber were considered.

Although the ABDB contains no specific entry for the bonding of butyl rubber to silicone rubber, it does indicate that silicone based adhesives are useful for bonding each of the materials. It is reasonable, therefore, to evaluate this class of adhesives along with appropriate surface preparation(s) for each of the adherends for the fabrication of such a laminate. The ABDB provides no guidance as to adhesives for bonding to fluoroelastomers. The literature, however, suggests that either epoxy or polyurethane based adhesives are useful for bonding to "properly treated" fluoroplastic surfaces. Because of the need for a highly flexible adhesive for this application, emphasis should be placed on the evaluation of polyurethane adhesives.

Proper surface preparation is the key step in the production of strong durable bonds. Surface preparations for butyl rubber run the gamut from simple surface cleaning and roughening to cyclization in strong acid to plasma treatment in air. This latter treatment is also effective for silicone rubber so that, in terms of process simplification, this one treatment should

2. KINLOCH, A. J. *Adhesion and Adhesives: Science and Technology*. Chapman and Hall, London, 1987.
3. LEE, L. H. ed. *Adhesive Chemistry: Developments and Trends*. Plenum, New York, 1984.
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7. GUTCHO, M. ed. *Adhesives Technology: Developments Since 1979*. Noyes Data Corp., Park Ridge, NJ, 1983.
8. *Military Standardization Handbook 691B: Adhesive Bonding*. 12 March 1987.
9. WEGMAN, R. F. *Surface Preparation Techniques for Adhesive Bonding*. Noyes Publications, Park Ridge, NJ, 1989.
10. PRANE, J. W. Consultant.
11. BODNAR, M. J. Chief, Adhesive Section, Picatinny Arsenal, NJ.

be evaluated for both of these adherends. If economics is the driver, separate, less complex treatments such as solvent wiping and surface roughening should be considered as well. The surface treatment of fluoroelastomers includes the so-called sodium etch which is widely used for fluorinated polymers such as PTFE, as well as the more straightforward solvent wiping and surface roughening.

A brief perusal of the literature provides no examples of the use of coupling agents for the enhancement of bonds to any of the substrates under consideration here. However, primers are discussed both for silicone rubber and for butyl rubber though not for fluorinated polymers. The primers are typically thin films or dilute solutions of the primary adhesive. As discussed above, a silicone adhesive may provide an effective primer for both butyl and silicone rubber. This should certainly be investigated. Alternatively, different appropriate adhesives for each substrate should be evaluated as primers with either then serving as the primary adhesive. The simplicity of using the same primer for both surfaces certainly is a major argument for the use of the silicone resin adhesive in this role. It should be noted that the use of a primer is not required. Because it adds to the complexity of the overall bonding process, a primer should be used only if it confers an essential improvement in the bond.

The sort of bonding process envisioned for the production of laminated materials of the sort under consideration here need not be complex. It is essential, however, that a great deal of attention be paid to details. The area in which the bonding operation is performed should be kept as clean as possible. The temperature and humidity should be carefully controlled. Especially harmful contaminants, such as release agents, oils, dust, etc., should be rigorously excluded from the area. (Ideally, a clean room should be utilized.) The process itself should be kept absolutely uniform, with no day-to-day variation in procedure, such as drying time for primer or cure time and/or temperature for bonding. Very tight quality control should be maintained on both the adhesives and adherends.

It is recognized that the sophisticated approach detailed above is expensive. This same approach is taken in the production of adhesive bonds in aerospace structures. In loosening the limits in some of these areas, it should be experimentally verified that neither the short term strength nor long term durability will be compromised.

Quality control or quality assurance encompasses a number of issues. As indicated above, the adherence to bonding procedures is a necessary condition for acceptable bonds; however, it is not sufficient. It is critically important that batch-to-batch variation in the adhesive be prevented. Such variation can effect strength and, more insidiously, durability, since the altered formulation may have different aging characteristics. Equally important is the prevention of variation in the adherends. Changes in formulation may affect their bondability. Clearly, a change in the nature of the base material could alter bondability, but so could a change in the kind or even the amount of an additive. This requires very tight specifications on the adherends, as well as the adhesives. These should be material specifications and not performance specifications. Without this level of control over composition, bond quality cannot be assured.

Bond qualification refers to the process of assuring that the bonded structure will perform as required, both initially and over time. It is crucial that testing which adequately reflects the end use environment, as well as application, be applied. Worst case scenarios should be considered, if only to help define the limits to which the bonds can be subjected. Contrary

to expectation, exposure to CWA liquids should not have much of an adverse effect on the bonds considered here. If well designed, they will have only minimum exposure to these liquids at their edges. By virtue of its essential function, diffusion to the bondline through the outer layer of the laminate should not be an issue.

The concept of multiple strippable layers does not appear feasible for the facepiece. This concept calls for incorporating inherently weak adhesive layers within the facepiece and/or barrier materials which can be easily torn. It is difficult enough to produce a single durable bond, but to assemble a system containing multiple, controlled, weak bonds seems next to impossible.

COATING/SURFACE MODIFICATION OF SILICONE

Improvement in CWA resistance may be achieved through surface modification and/or coating of the silicone. A thorough study was conducted by Dow Corning¹² in which changes in the siloxane backbone were made to improve CWA resistance. However, these materials showed inferior mechanical properties relative to silicone. It should be possible to preserve the favorable bulk properties of the silicone while improving barrier properties by chemically modifying the silicone surface to resemble alternative polysiloxanes. However, this approach is severely limited by the physiochemical nature of the generic siloxane backbone.

The penetration of CWA's through barrier materials generally proceeds via two distinct steps. The first is the introduction of the CWA molecules into the barrier material from an external reservoir. The second consists of the transport of these molecules through the barrier material by diffusion. The first step is governed by thermodynamics (CWA/CWA interaction versus CWA/polymer interaction, surface energy and contact angle, etc.), while the second depends for the most part on concentration, free volume, and polymer segment mobility. While the chemical modification of silicone can greatly influence the rate of the first step, it may have little or no effect on the second.

Silicone rubbers consist of a semi-ionic (ca. 50% ionic) Si-O backbone shielded by non-polar methyl groups. The Si-O bonds are relatively long and the Si-O bond angle is large. Rotation about these bonds and the Si-C bonds is free of restriction. It is the free rotation of the methyl groups about the Si-O backbone which shields it and results in the non-polar nature and low surface energy properties of silicone rubbers.

CWA's are generally of intermediate polarity. The initial penetration of CWA's into silicone is somewhat restricted by the surface properties imparted by the freely rotating methyl groups. However, once the CWA molecules have crossed the CWA/silicone interface, the large free volume in the vicinity of the Si atom and freely rotating methyl groups present the penetrating molecules with an open door. Diffusion proceeds virtually unimpeded.

Theoretically, it should be possible to decrease the Si-C and Si-O bond lengths, and perhaps to limit rotation, by adding electron withdrawing species to the methyl groups. However, in reality, this cannot be done without destabilizing the polymer. In the past, there has been some success in improving the barrier properties of siloxane rubbers by replacing the

12. POLMANTEER, K. *Lens Elastomer Optimization Progress for New Protective Mask, XM30*. Dow Corning Corp., Midland, MI, June 1981

methyl groups with electron withdrawing fluoroalkyl groups. These polymers are only stable if the fluorinated moiety is separated from the siloxane by a spacer unit which is at least two methylene units long. This apparently explains the failure of fluorine (CF₄) plasma treatments in improving the barrier properties of silicone. The decrease in the permeability of siloxane fluoropolymers can be attributed mainly to increased shielding of the siloxane backbone and decreased surface energy. While both factors decrease the rate of the first step of CWA penetration, diffusion, controlled by free volume and segment mobility, is probably unaffected. In fact, the free volume of these polymers is usually increased by the increasing bulkiness of the substituent group.

Similarly, attempts to inhibit free rotation by the substitution of bulky groups for the methyls may not only have limited success, but will also invariably result in increased free volume. Further, any attempt to suitably improve barrier properties by radiation or plasma crosslinking of the surface, would require such extensive crosslinking as to embrittle the surface beyond use.

Overall, chemical modification would not appear to be an effective means of improving the barrier properties of silicone. Plasma and ion fluorination of other synthetic rubbers¹³ provided only temporary improvement in absorption rate for the plasma treatment and led to embrittlement and cracking for the ion implantation technique.

The problems in surface coating silicone to improve barrier properties are essentially identical to those encountered in adhering a suitable barrier material to a silicone surface, except in the coating case the adhesive is also the barrier. No coatings exist which adhere to the unmodified silicone surface, unless the coating is itself a silicone. Surface preparation is thus necessary and would follow similar methods as described for adhesive bonding preparation.

It is possible to introduce functionalities into the silicone, either during polymer formation or by surface modification, which enhance adhesion through the formation of chemical bonds. In order to maintain the desired properties of the silicone, chemical modification of the silicone surface would be the preferred route. Reactive functionalities, such as hydroxyl or amine, are recommended due to ease of incorporation, diversity of possible reactions with candidate coatings, and stability of the resultant modified siloxane (hydroxyls and amines are non-electron withdrawing). Hydroxyl groups can be introduced either by mild hydrolysis of the siloxane backbone or by oxidation of the methyl groups. Amine groups are best introduced by halogenation followed by reaction with ammonia. Other possible methods for functionalizing the silicone surface include replacing the methyl groups by electrophilic substitution and the use of mild hydrolysis followed by reaction with functionalized siloxane surface agents.

COPROCESSING WITH SILICONE

Improvement in CWA resistance may be achieved by coprocessing silicone with better resistant materials. Processing elastomeric materials consists of forming the product from uncured material then crosslinking the material into the final form. Coprocessing of a laminated material can proceed by three distinct routes: lamination of two completely

13. LEGG, K. O. *Plasma and Ion Fluorination for Chemical Hardening of Synthetic Rubbers*. U.S. Army Materials Technology Laboratory, MTL TR 89-92, October 1989.

cured/formed materials, lamination of an uncured material to a formed uncured or cured material followed by cure of the final product, and lamination of two uncured materials followed by formation and cure of the final product. The first process is essentially adhesive bonding. The second process would include coating, but also includes other sequential processing methods. This section will primarily consider the methods of the third processing route and address the other sequential methods. The adhesive bonding and coating methods have been covered above. As in the adhesive bonding section, the lamination of butyl/chlorobutyl rubbers and fluoroelastomers with silicone were considered.

Currently available silicone facepiece components are injection molded which allows for the production of complex shapes. Either injection molding or transfer molding allows for sequential processing of laminated facepiece by using a premolded form of one material as insert for molding of the second material. However, all the same problems encountered with adhesive bonding and coating also apply. The premolded material requires similar surface treatment before the addition of the second material to assure a durable bond in the final laminated product. Rotational molding might also be used for the sequential molding of a second material over an insert.

Concurrent formation of an uncured laminated material avoids the problems and additional processing time associated with the surface preparation of sequential processing methods. Interpenetration of the two materials before cure should provide a stronger laminated material. However, this interdiffusion will most likely be limited. Strength of this interface can be enhanced by the incorporation of compatibilizers. These are typically copolymers similar to the two incompatible materials to be joined. Once they migrate to the interphase, the copolymer components associate with their corresponding pure phase and chemically linked with it if desired. Chung and Hamed¹⁴ recently reported on work with a butyl rubber/nitrile rubber system where a copolymer was formed at the interface after the faster migration of the low molecular weight components of the copolymer.

Compression molding or another thermoforming technique consisting of a cocatalyzed or coextruded sheet material could be utilized for the concurrent formation process. Careful selection of the individual cure systems must be made to assure compatible processing behavior. An undeveloped possibility is the rotational molding of two liquid systems with separation in the mold by centrifugal force.

ALTERNATIVE DESIGNS

The various approaches considered to this point all assume that a laminated material of silicone with a CWA resistant material would yield improvements to the current facepiece design. This material would ideally maintain the wearability of silicone and the CWA resistance of butyl rubber or fluoroelastomer. However, the mechanics of the design must also be considered. A desired physical property must also be associated with the type of deformation it undergoes. Wearability of the facepiece is associated with stretching, compression, and shearing of various sections. These deformations would also occur both parallel and perpendicular to the laminate surface.

14. CHUNG, M. H., and HAMED, G. R. *Rubber Chem. Technology*, v. 62, 1989, p. 367.

If a laminate is stretched parallel to its surface, the stiffer material will dominate. If the same laminate is stretched perpendicular to its surface, the softer material will dominate. So wearability of a laminate is not necessarily guaranteed if one of the layers is considered wearable. Thus, assigning engineering specifications for the entire facepiece, as in Table 1, may not reflect the engineering requirements for the different sections of the design. The purpose of this alternative design approach was to consider how currently available materials may be better incorporated into the facepiece rather than the current design.

The goal of any facepiece system is to provide the head with CWA protection and do it comfortably. The soldier must be able to breathe, see, and hear. This does not necessarily have to be achieved through the use of a tightly fitted facepiece. A butyl fabric hood is presently used to cover most of the head. Any impermeable material (including thermoplastics, glasses, etc.) can be used in a hood arrangement over the entire head with the provision for vision. There is no requirement for the breathing apparatus to be attached to the head, only to supply air under the hood. If fit to the face is required, it can be done with an all silicone system under the impermeable material.

More specifically to the present facepiece design, an all butyl facepiece with some type of silicone O-ring under it around the face may provide a better seal than a laminate. The loss in the flexibility of the facepiece can be made up with an all silicone back-strap piece which now resides under the butyl fabric hood. The correct material selection for where it is required would seem to provide a number of options, even in the current design, provided the engineering specifications are not applied where not needed.

ALTERNATIVE MATERIALS

Previous studies on butyl rubber and fluoroclastomers show excellent CWA resistance. Other elastomeric materials may also prove valuable, but their CWA resistance is not yet documented. The incorporation of silicone into blends, interpenetrating networks (IPN's), and/or copolymers were considered along with some experimental materials which may not make the required 6.3 implementation by FY1994.

Polymer blends have been investigated to some extent.* The findings observed to date accurately reflect the benefits and limitations of conventional blends. The properties of the blend are essentially a mixture of the properties of its components. The contribution of each component to the final properties of the blend is roughly proportional to the percentage of the component present. Thus blending an agent resistant material into the silicone compound more or less linearly degrades mechanical properties as it enhances barrier properties. This approach is likely to yield at best a compromise material which falls short of all the desired specifications. There is the possibility that a complex ternary or quaternary blend could result in an improved material, but the complexity, expense, and time required to perform such a blending study make this a poor prospect for a solution to the current problems.

IPN's can be regarded essentially as high performance blends. Their chief advantage over blends is their superior uniformity and homogeneity. This leads to superior performance compared to conventional blends, particularly in the areas of strength and durability. The effect

*GROVE, C. Memorandum for Record.

of the best IPN's is to achieve blending at the molecular level. This results in a material with properties that are a hybrid of its components, but in which the properties of the pure components are hidden. A typical example is that of an IPN incorporating two components: one with a high glass transition temperature and one with a low glass transition. In a well formed IPN, the resultant material exhibits one broad glass transition somewhere between those of the components. Again, it is unlikely that this technology will result in a satisfactory material since incorporation of an effective barrier material is expected to have a detrimental effect on the mechanical and low temperature properties of the product material. Sperling¹⁵ discusses IPN's containing silicones. Commercial IPN's containing silicone are available from Petrarch Systems and Uniroyal. A number of functionalized silicones are available from Petrarch Systems for incorporation into IPN's or copolymers.

In the past few years it has been demonstrated that block copolymers of siloxanes with hydrocarbons can give rise to unique morphologies in which the respective blocks orient themselves into layered structures when processed. Work by Arnold et al.¹⁶ with polyimide-siloxane (PI-PSX) block copolymers exhibit this effect. In PI-PSX copolymers with 10% to 20% siloxane blocks, a surface layer forms that is 80% siloxane. The result is a high temperature polymer with the structural properties of polyimide and a hydrophobic surface typical of the siloxane. This effect greatly enhances the stability of the polyimide to environmental degradation. Work with a catalytic hydrosilation crosslinking process that could conceivably be applied to produce siloxane-butyl block structures is being investigated at Dow Corning. Assuming that a PSX-butyl copolymer would demonstrate the same properties as the PSX-PI polymers of Arnold, then one might expect to form a butyl material with a siloxane-rich surface. While such a material probably would not have the necessary mechanical properties required to produce a monolithic facepiece molding, the approach might be used to produce a butyl layer that is surface compatibilized with the siloxane facepiece so as to facilitate adhesive bonding or co-molding in order to permanently fuse a barrier layer to the facepiece.

Carbonyl containing compounds are good solvents for silicone polymers, and this may be so due to interactions between the carbonyls and the Si-O backbone. Intimate interactions of this kind may, to some extent, result in a reduction of free volume. If this is so, then the incorporation of short blocks of keto-polymer or keto-fluoropolymer into the silicone may be a way of decreasing free volume and possibly of hindering the free rotation of the siloxane alkyl substituents.

Another class of copolymers with potential for this application is the thermoplastic elastomers (TPE's), typified by the Kraton line of products from Shell. Although these materials have apparently received some consideration as a barrier film to be applied over the silicone facepiece, there is no indication that making the facepiece entirely out of TPE's has been considered. It may be worthwhile to note that two new Kraton compounds have recently been developed which have mechanical properties very similar to (and are intended to compete with)

15. SPERLING, L. H. *Interpenetrating Polymer Networks and Related Materials*. Plenum, New York, 1981

16. ARNOLD, C. A., SUMMERS, J. D., and MCGRATH, J. E. *Poly. Eng. Sci.*, v. 29, 1989, p. 1413

silicones. A recent publication¹⁷ reviews some of the properties of these materials. Monsanto is also currently working on a butyl TPE which shows good permeation resistance. If all mechanical properties fall in an acceptable range, the TPE's are virtually certain to offer enhanced agent resistance relative to silicones.

Some experimental polyurethanes hold promise as potential facepiece materials or coatings. One of the best might be an experimental polyurethane formed with hydroxyl terminated isobutylene telomers.¹⁸ Properties of this butyl rubberlike material can be varied by changing telomer lengths and isocyanate structure. In addition, the isocyanates react readily with hydroxyl and amine functionalized surfaces. Similarly, another potential candidate might be an experimental polyurethane formed with hydroxyl terminated polyethylene. Preliminary investigations on this material are being carried out by Catherine A. Byrne at U.S. Army Materials Technology Laboratory (MTL).

Other potential facepiece materials include fluorophosphazenes and some new low temperature fluoroelastomers from Dupont.

SUMMARY

For a facepiece design similar to the one currently used, the ideal facepiece material would be a homogeneous elastomer which fits all the criteria for CWA resistance, wearability, and aging/storage behavior. With only limited CWA resistance information available, this ideal material does not appear to currently exist. The best alternative seems to be a different design using currently available materials. CWA resistance can presently be achieved, but the combination with wearability typically eliminates a material from consideration. An alternate design with available materials should yield an acceptable combination. If a laminate can provide the wearability that is required, either the coextrusion/cocalendering or the adhesive bonding of a butyl/silicone material should provide another option.

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17. METZLER, E. S. *Rubber World*, v. 199, 1988, p. 38.

18. IVAN B., and KENNEDY, J. P. *Proc. ACS Div. Poly. Mat. Sci. Eng.*, v. 58, 1988, p. 869.

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